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HIGH FLUX, FOULING RESISTANT MEMBRANES FOR RO PRETREATMENT

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14. ABSTRACT

High Flux, Fouling Resistant Membranes for RO Pretreatment, is contract number N00014-10-C-0224. The purpose of the contract is to develop pretreatment membranes that improve the desalination process onboard ships. In the case of pretreatment, this means extending the life of the RO membranes and improving the reliability (uptime) of the desalination process. The scope of the contract as proposed by PoroGen and Clean Membranes is to develop a fouling resistant, hollow-fiber, ultrafiltration membrane. Activities in the second 3 months of the project included:
1. completing the set up of production and lab areas for the project,
2. preparing and testing flat sheet membrane with actual raw materials to be used for production to replicate flux and fouling resistance performance achieved with lab scale materials,
3. spinning initial PAN based hollow fiber to establish baseline spinning condition, varying parameters such as spin dope composition, temperature, and spinneret air gap, and

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Abstract

High Flux, Fouling Resistant Membranes for RO Pretreatment, is contract number N00014-10-C-0224. The purpose of the contract is to develop pretreatment membranes that improve the desalination process onboard ships. In the case of pretreatment, this means extending the life of the RO membranes and improving the reliability (uptime) of the desalination process. The scope of the contract as proposed by PoroGen and Clean Membranes is to develop a fouling resistant, hollow-fiber, ultrafiltration membrane.

Activities in the second 3 months of the project included:

1. completing the set up of production and lab areas for the project,
2. preparing and testing flat sheet membrane with actual raw materials to be used for production to replicate flux and fouling resistance performance achieved with lab scale materials,
3. spinning initial PAN based hollow fiber to establish baseline spinning condition, varying parameters such as spin dope composition, temperature, and spinneret air gap, and
4. configuring and running preliminary test equipment for the hollow fibers.

Summary of results:

1. PAN hollow fibers produced with various PAN raw materials demonstrated improved mechanical characteristics suitable for hollow fiber membranes.

2. Bench tests for flux and fouling resistance verify that the membranes produced now are comparable in performance to work done initially at MIT.

Future work includes:

- Optimize PAN-based hollow-fiber spinning conditions.
- Incorporate PAN-g-PEO into PAN membranes
- Development of cross-flow testing methods
- Fouling and retention testing in cross-flow configuration
- Module design and fabrication
- Large-scale testing

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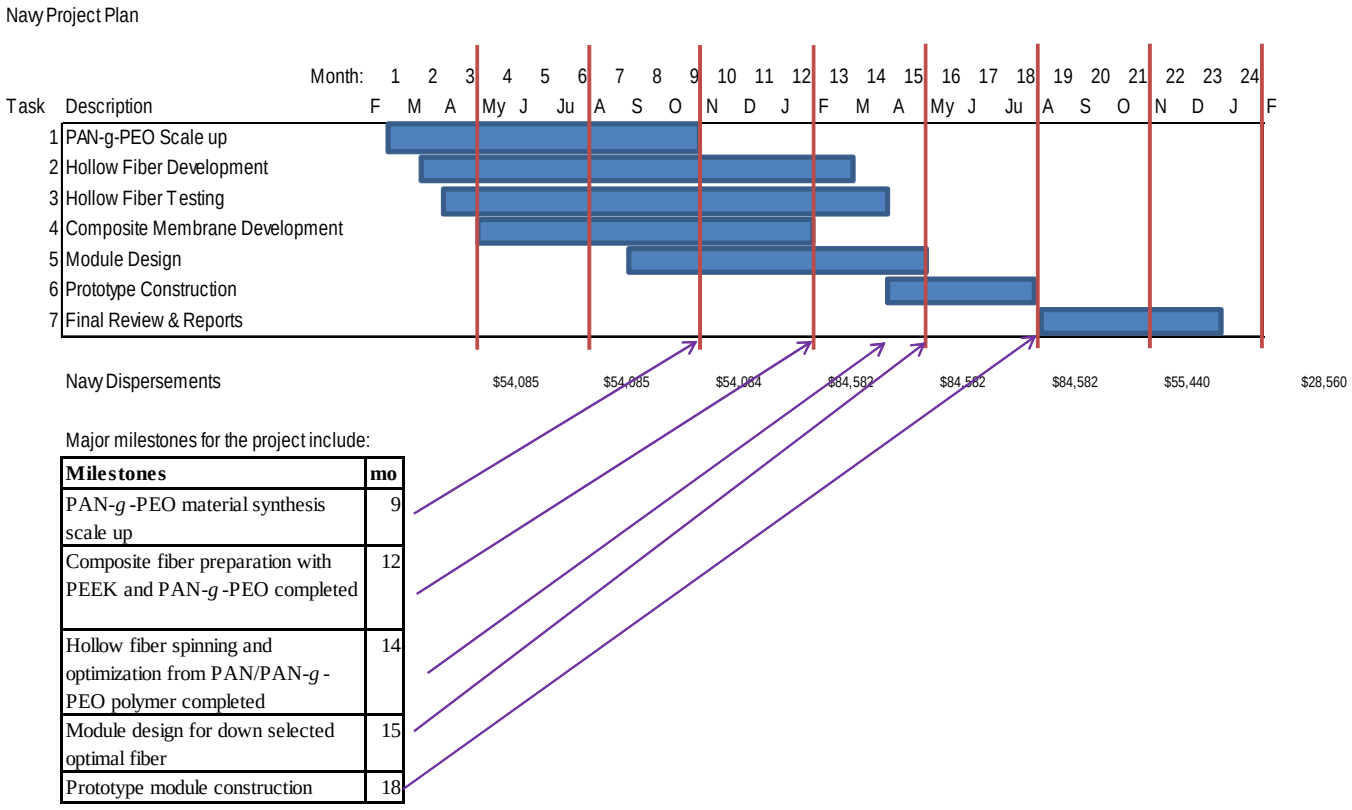
Summary

Contract number N00014-10-C-0224 is a joint project between Clean Membranes and PoroGen. The project objective is to develop low-maintenance, high-flux, low-fouling water filtration modules for reverse osmosis (RO) pre-treatment in order to improve the desalination process onboard ships. Membrane modules developed in this project promise to exhibit improved flux and fouling resistance. This in turn will lead to more compact and efficient filtration systems that reduce maintenance and downtime, costs and energy requirements.

The project brings together the unique capabilities of PoroGen and Clean Membranes. PoroGen provides state-of-the-art hollow fiber membrane and module development expertise that will be combined with Clean Membranes' high flux, fouling resistant membrane technology developed at MIT. Two types of membranes will be developed: (1) a pure PAN/PAN-*g*-PEO polymer membrane, and (2) a composite PEEK – PAN/PAN-*g*-PEO membrane. At the end of 18 months of development, the project will have selected the most suitable membrane for Navy application and have designed and developed a prototype module for testing in Navy's FNC desalination system.

The tasks, schedule and milestones are as indicated in Figure 1. This progress report summarizes the work in the second quarter of the project that addressed Tasks 1, 2 and 3, with initial work for Task 4 initiated. The production of the PAN-g-PEO co-polymer was successfully scaled up to produce a 1 kg batch in the first 3 months. Initial hollow fiber was spun with various grades of PAN, giving us a good basis for suitable hollow fiber. The same raw materials were used to create flat sheet membrane. Testing apparatus has been assembled to test both fibers and flat sheet produced with the raw materials synthesized in commercial setting and initial results verify performance consistent with original bench-scale work at MIT.

Figure1. Navy Project Plan



Milestones	mo
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Module design for down selected optimal fiber	15
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Introduction

Current Navy desalination technology utilizes the Navy Standard Reverse Osmosis unit (NSRO) where cartridge filters are the pretreatment prior to single pass reverse osmosis. The NSRO system was designed in the 1980's for mainly open ocean use and expected RO membrane life of 3-5 years. Now that the ship deployments are closer to shore and the pollutants are moving further out to sea, actually membrane life is reduced to as little as 4-8 weeks when in turbid waters. This affects current operations by requiring frequent and costly membrane replacement, leads to reduced reliability, increases maintenance and the space requirements to store replacement modules.

Pretreatment prior to the reverse osmosis membranes is a standard practice in industrial applications to extend the reliability and life of the RO. However, current commercial ultrafiltration and microfiltration membranes used for RO pre-treatment are inadequate and subject to fouling by particulates, organics and other dissolved components. The filters are irreversibly fouled, resulting in a dramatic decline in flux requiring frequent cleaning, maintenance and down time. The build-up and deposit of dissolved and suspended solutes near and onto the membrane surface, termed concentration polarization, is another serious limitation that also aggravates fouling.

Clean Membranes technology employs combination of PAN and PAN-g-PEO co-polymer. The hydrophobic backbone of PAN and the hydrophilic nature of the PAN-g-PEO co-polymer provide a strong porous membrane that resists fouling by repelling the pollutants and preventing adsorption of foulants. During the course of this project we will scale-up the technology and manufacture a hollow-fiber module that may be used for pretreatment to the reverse osmosis unit in the Navy desalination system.

Methods, Assumptions and Procedures

PAN-g-PEO synthesis

To produce the PAN-g-PEO copolymer all reagents were purchased from Aldrich and used without further purification. Polyacrylonitrile-graft-poly(ethylene oxide) (PAN-g-PEO) was synthesized by free radical polymerization. PEO content of the copolymer was determined by 1H nuclear magnetic resonance (NMR) spectroscopy in deuterated DMSO. The molecular weight distribution of the polymer was determined by gel permeation chromatography in DMF.

Flat Sheet Membrane Casting and Testing

As a model system to characterize starting materials, flat sheets were prepared prior to hollow fiber spinning. Flat sheet membranes were cast following the procedure described in Asatekin *et al., Journal of Membrane Science*, 298 (2007) 136-146. In brief, both polymers were dissolved in dimethyl formamide (DMF) at 12% (w/v) concentration. Then, the two solutions were mixed in a 4:1 PAN:PAN-*g*-PEO ratio. The solution was filtered through a 1 µm glass fiber filter and degassed by heating. The solution was cast onto a glass plate using a doctor blade nominally adjusted to 200 µm, and the plate was immersed into distilled water at room temperature. After ~15 minutes, the membrane was moved into a fresh water bath for at least 24 hours. The membranes were annealed by heating to 90^{o}C for 4 hours.

Flat sheet membrane performance is evaluated by measuring flux and rejection. The equipment for testing flat sheet and hollow fiber membranes is described in detail in the following section. Flat sheet testing was performed using a circular membrane sample 25 mm in diameter, in an Amicon 8010 dead-end stirred cell (Millipore). For the test, first distilled water was filtered through the membrane at ~6.5 psi for 1 hour. Both the pressure and the filtrate weight was recorded every 2 minutes. Then 10 mL of 1000 mg/L bovine serum albumin (BSA) in phosphate buffered saline (PBS) was loaded into the filtration cell. The filtration was continued for 20 min, with water still in the feed reservoir. As BSA is largely retained by this membrane, a significant BSA concentration is present on the membrane throughout the test. Finally, the membrane and cell was rinsed with water. Water flux was measured again.

The use of surrogate soluble polymers is an industry wide standard procedure for membrane performance evaluation. The polymer marker selection is carried out to provide good representation of foulants encountered in actual sea water. Basic performance criteria for future testing will include water flux and retention of bovine serum albumin (BSA) as a benchmark of pore size, and resistance to

protein fouling by BSA filtration. We plan to use synthetic and actual sea water feeds for membrane characterization in final stages of membrane development.

Hollow Fiber Development and Testing

Design of experiments is used to optimize membrane preparation procedures. The design parameters include Solvent selection, solids content, PAN-g-PEO/PAN ratio, additives that include porogens and surfactants and hollow fiber spinning procedures that include air gap, spin dope temperature, bore fluid selection and coagulation bath temperature and composition.

Hollow fibers are produced by accepted hollow fiber membrane manufacturing process – dry wet spinning process.

Hollow fibers were tested using the following method: Four fibers were cut to 45 cm length and potted in polyethylene tubing using low temperature adhesive (3M 3972LM). Potted fibers were soaked in water for at least 24 hours to remove any residual preservatives. Fiber modules were gently blotted dry and attached to the test rig. Water was then applied at the specified pressure, and allowed to equilibrate for 20 minutes. During each test, filtrate was collected in a beaker for a specified time and the mass of the filtrate was measured. Two replicate segments were tested from each membrane.

Results and Discussion

Three tasks were addressed during the first 3 months of work and the results are summarized below:

Task 1. Material Preparation and Scale Up of PAN-g-PEO Co-polymer

The objectives of the scale-up were (1) to produce material for hollow-fiber spinning and (2) obtain initial material property data to facilitate further performance optimization. Our efforts addressed both objectives, though emphasis was placed on material production to enable hollow fiber spinning.

Several specialty polymer synthesis firms were contacted, bids obtained and a contract negotiated for production of one kilogram of the PAN-g-PEO material. PAN-g-PEO polymer was synthesized following the method developed by MIT team < Asatekin, JMS 2007> by the outside vendor, and data were collected regarding composition, purity and molecular weight of the product.

Figure2. Certificate of Analysis for PAN-g-PEO copolymer

CM-Tec

CM-Tec, Inc.
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04/09/10

GPC Analysis

Running setup:

Mobile phase: HPLC grade DMF in a flow rate of 1.0ml/min.
Column: Linear mixed-bed column with a MW range of 1k – 5,000kDa.
Detector: RI.
Standards: Polystyrene.

Results:

Mw = 1140 kDa, Mn = 780 kDa, PDI = 1.5

^{1}H-NMR Analysis

Solvent: d-DMSO

PEG molar number: X
AN molar number: Y

2X = 1.0
X + Y = 6.569 – 1.424

X = 0.5
Y = 4.645

Wt% of PEG: 0.5 x 480 / (0.5 x 480 + 4.645 x 53) x 100% = 49.4%

PAN/PEG = 50.6/49.4 by weight.

These results constitute an important program milestone: ***It was demonstrated that the PAN-g-PEO polymer can be produced on commercial scale.*** Production of this first lot demonstrates that the underlying chemistry is suitable for industrially relevant polymerization processes. In addition, this first lot provides a benchmark for subsequent lots. Based on these analyses, material produced in this first polymerization is suitable for making PAN-g-PEO based membranes. This task is completed ahead of schedule.

Task 2. Hollow Fiber Membrane Development

Work is ongoing to experiment with production techniques to optimize fiber development.

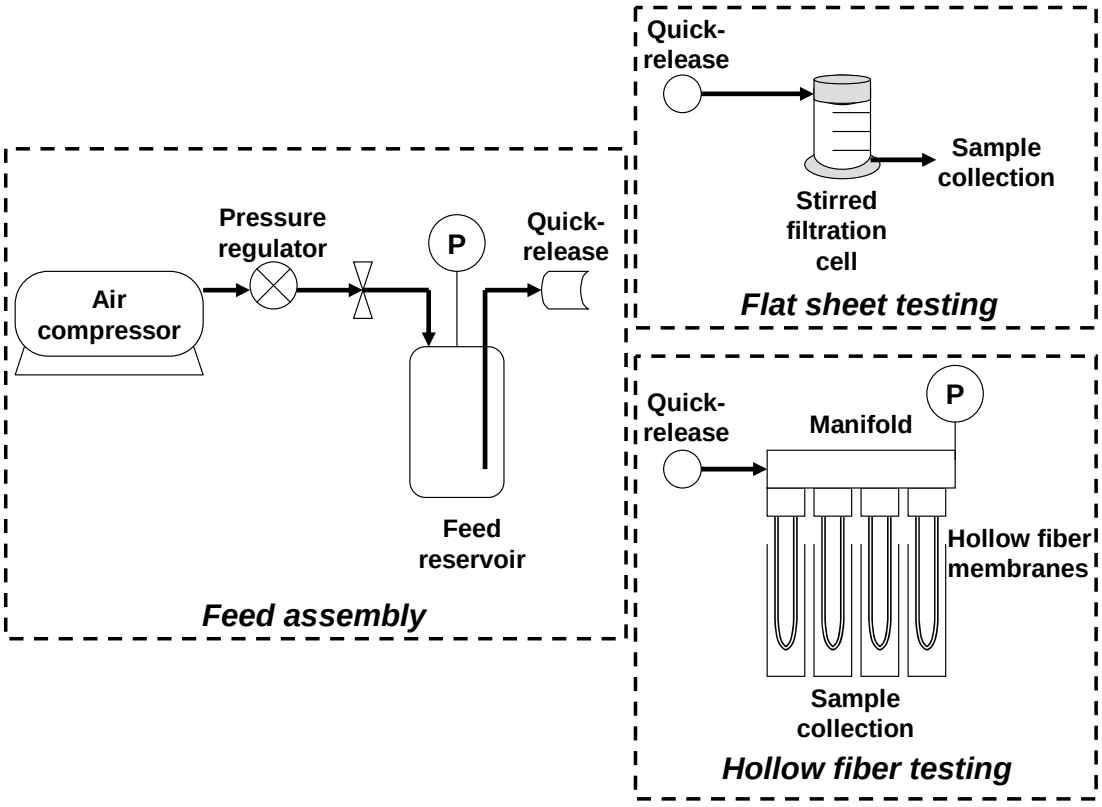
The dry-wet spinning line was reconfigured for spinning of PAN-g-PEO/PAN blends. The spinning line consisted of spinning dope delivery system that included pump, filters and control equipment, bore fluid injection and metering system, spinneret, coagulation tank and related take up equipment. A mixer for spin dope preparation was procured to address anticipated viscosity ranges and material rheology. The spinning system was base lined utilizing spinning dopes based on PAN polymer. Several PAN polymer grades were evaluated. Initial hollow fibers were produced utilizing a matrix of spinning experiments that included spinning temperature, air gap and draw ratio. Following these procedures, we produced a series of water permeable PAN hollow-fiber membranes. These membranes had sufficient mechanical strength to be shaped, and were successfully potted into test modules.

Task 3. Hollow Fiber Membrane Performance Testing

Lab space was acquired and materials were assembled to begin membrane performance evaluation in support of membrane development. The lab equipment was designed to accommodate flat sheet membranes as well as hollow fibers.

The equipment consists of three modules (Figure 3). The feed assembly is used in all tests, whereas two modules, one for flat sheet membrane testing and the other for hollow fibers, can be exchanged easily through the use of quick release connections. The feed assembly uses an air compressor equipped with a pressure regulator to pressurize feed liquid (i.e. water, foulant solution, etc.) contained in a dispensing reservoir. We intend to use pressures between 5-10 psi for the testing of UF membranes, as these are industrially relevant pressure differences. However, the system is equipped to handle as high as 75 psi.

Figure 3: Schematic of membrane test equipment



Flat sheet testing was done using a dead-end stirred cell, manufactured by Millipore (Amicon model 8010), attached to this feed assembly. The hollow fiber test module is currently equipped to test four dead-end type membrane modules at a time. It can also be modified easily to perform cross-flow tests, and can be expanded in series.

Flat sheet testing is important especially in the initial stages of membrane development, because PAN/PAN-*g*-PEO blend UF membranes are well characterized in flat sheet format. Previous peer-reviewed publications have documented performance of these membranes as well as the influence of some casting parameters (blend composition, copolymer composition) on membrane performance. Hence, preliminary testing of flat sheets is an important benchmark in evaluating specific casting parameters, especially variations in materials such as the grade/purity/manufacturer of PAN, PAN-g-PEO, solvents and other additives.

During this reporting period, the first set of tests were performed with such flat sheets, to confirm that the industrial grade raw materials used would result in performance comparable with those observed in lab studies at MIT. Key results in this study were high flux (up to 1500 L/m^2.h.MPa, Asatekin *et al.,*

Journal of Membrane Science 298 (2007) 136-146), and complete resistance to irreversible protein fouling, as evidenced by complete flux recovery by a water rinse.

During the first reporting period, three commercially available PAN grades were identified. These were all fibers made of copolymers of PAN with other monomers, and were identified by their PAN content as 98%, 93% and 60%. 98% PAN samples were found to yield quite unsatisfactory hollow fibers in preliminary tests. 60% PAN, on the other hand, can potentially lead to heterogeneities when blended with PAN-*g*-PEO during casting, due to potential incompatibility of the components. Therefore, 93% PAN was selected to conduct the initial flat sheet membrane casting and testing experiments.

Another important parameter is the performance of PAN-*g*-PEO that was manufactured in commercial scale. As discussed in the previous reports, PAN-*g*-PEO that was manufactured in a kg-scale batch had a significantly higher molecular weight than used in MIT studies. It was important to ensure this did not result in decreased performance.

Flat sheet membranes were cast from blends of 93% PAN and commercial grade PAN-*g*-PEO following the procedure described in Asatekin *et al., Journal of Membrane Science*, 298 (2007) 136-146, and in the previous section. The resultant membranes appeared physically very similar to membranes cast from research grade PAN and small-batch PAN-*g*-PEO. However, to ensure the performance is comparable to previously tested membranes, a filtration test was conducted (see Methods).

During the test (Figure Y), the water flux through the membrane initially decreases due to the compaction and compression of the membrane material, a phenomenon well-documented for all porous membranes. The pure water permeability of the membrane stabilized at 710±100 L/m^2.h.MPa. The error margin arises due to the limitations of the measurement setup and will be improved further by automating and enhancing sample collection procedures. This value is lower than that observed in previous PAN-*g*-PEO tests, however it is still quite high for UF membranes. It should be noted that the pore size of this membrane was not measured, and could potentially be significantly smaller. This measurement will be performed in the next reporting cycle.

Then the fouling propensity of this membrane was measured, by filtering 10 mL of 1000 mg/L BSA solution followed by dilution with water. During this test, the flux through the membrane did not decrease, and averaged 730±100 L/m^2.h.MPa. This indicates a very strong resistance to fouling. Upon switching back to water, the flux through the membrane remained the same. The results of this test can be seen in detail in Figures 4 and 5.

Figure 4: Change in the permeability of PAN/PAN-*g*-PEO blend membrane manufactured from commercial raw materials during a fouling test.

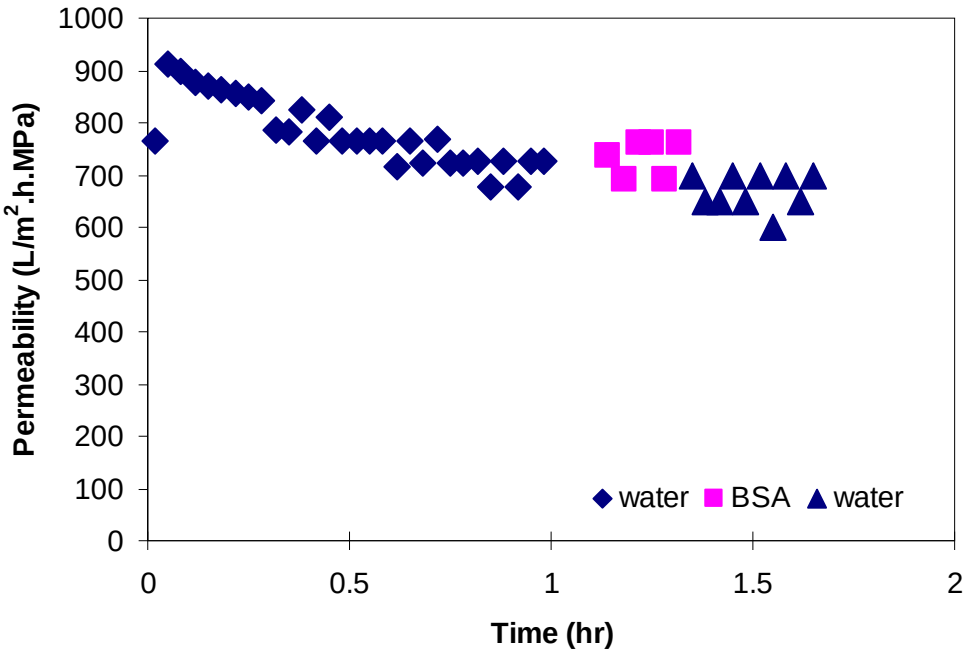
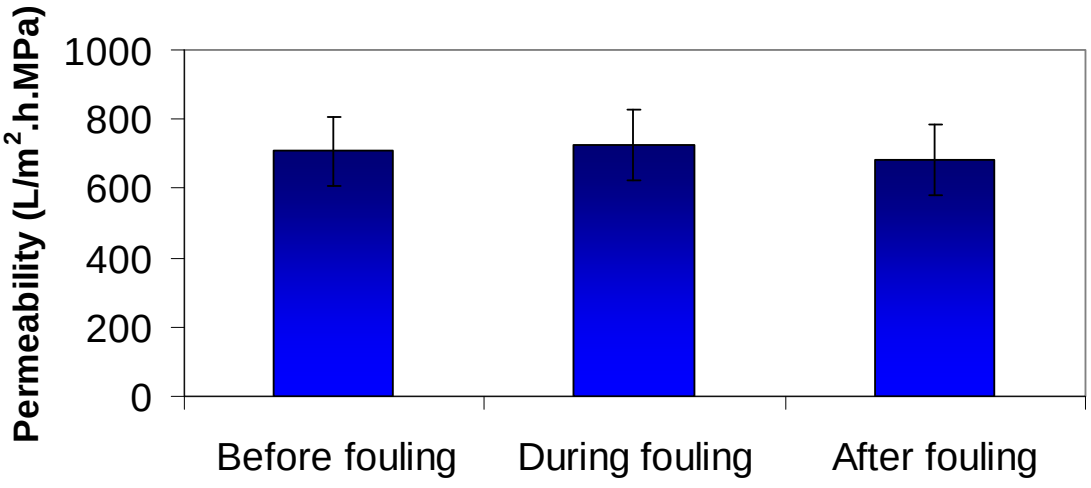


Figure 5: Permeability of PAN/PAN-*g*-PEO blend membrane manufactured from commercial raw materials before, during and after fouling with a protein.



This data is very significant in proving that ***the superior performance of PAN/PAN-g-PEO blend membranes, to date reported only with research-grade, high purity ingredients, can be reproduced***

using commercial grade raw materials. This is crucial in the future scale-up of these membranes, as large scale manufacture from high purity, high cost ingredients would be cost-prohibitive.

This data also confirms that commercial production of PAN-*g*-PEO was successful. The kg-scale batch manufactured satisfies not only the preliminary parameters of composition, molecular weight and purity, but also produces high-performance, fouling resistant membranes.

The flat sheet tests reported here aimed to simply confirm two main criteria: High flux, and protein fouling resistance. Future testing will also aim to characterize the pore size of these membranes. This set of experiments proved to be a good indicator of membrane performance as well as brush structure in previous studies on flat sheet membranes <Asatekin JMS 2007, Kang JMS 2007>. Protein fouling experiments were also indicative of fouling resistance to other feeds, such as bacteria suspensions <Adout ES&T 2010> and oily wastewater <Asatekin ES&T 2009>.

Hollow fiber testing equipment, as described earlier, is also now in working order. Hollow fibers will be characterized as described above as well. However, the geometry of these fibers will require cross-flow operation for most fouling tests. As a screening tool, static fouling experiments are being considered. In such experiments, the modules will be prepared in a dead-end configuration. The pure water flux through the membrane will be measured. Then the membrane will be immersed in a protein solution overnight, and water flux will be measured again after rinsing it briefly.

Preliminary hollow-fiber membranes' testing was performed using the test apparatus as described in the Methods section. Fibers were mechanically durable, and were readily assembled into modules. No brittleness or cracking was observed. Fibers adhered firmly to the module inlet, and were stable up to 10 PSI. These membranes were in-process samples produced to evaluate the hollow-fiber spinning setup, and have not been optimized for flux. All membranes tested showed fluxes around 1 g/min per test module. These results demonstrate the suitability of our hollow-fiber casting process for creating water permeable PAN membranes. This method has been developed to be compatible with PAN-g-PEO membrane casting, and incorporation of the copolymer is not expected to introduce any significant complications. In addition to demonstrating the efficacy of the casting process, these results indicate that suitable testing apparatus and methods have been devised. Furthermore these results demonstrate that our current test module fabrication process is suitable for producing mechanically sound modules. Experience gained in test module fabrication may lay the foundation for full-scale module development. Work is ongoing to optimize PAN hollow-fiber membrane casting and to incorporate PAN-g-PEO into the polymer feed.

Task 4. Composite Membrane Development

Preparation of composite membrane based on porous PEEK hollow fiber substrate was initiated. The casting line for composite membrane preparation available at PoroGen was reconfigured to accommodate PAN-g-PEO solvent system characteristics. Initial casting runs will be conducted next quarter.

Conclusions

With the production of the co-polymer we conclude that the synthetic method used to produce PAN-g-PEO can be scaled beyond the lab bench and the underlying chemistry is suitable for industrially relevant polymerization processes. We also conclude that it is possible to manufacture high flux, fouling resistance membranes comparable in performance to previous studies using commercial grade PAN and PAN-*g*-PEO. We have demonstrated the ability to produce water-permeable hollow-fiber membranes, a critical step in developing modules. These membranes were successfully assembled into test modules, and showed a stable pure-water flux under relevant pressures.

Recommendations

None

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List of Symbols, Abbreviations and Acronyms

FNC: Future Naval Capabilities

ONR: Office of Naval Research

PAN: Polyacrylonitrile

PAN-g-PEO: Polyacrylonitrile-*graft*-polyethylene oxide

RO: Reverse Osmosis

NSRO: Navy Standard Reverse Osmosis technology

UF: Ultrafiltration

BSA: Bovine serum albumin

PBS : Phosphate buffered saline

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